Meeting Circular Economy by producing leather from (*sarda sarda*) fish

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Abstract

Following the principles of circular economy and waste reduction, recycling fish skin is an interesting and sustainable practice. However, traditional tanning procedures give rise to many sustainability concerns throughout the process. The most serious of these is chemical pollution as traditional tanning frequently uses harmful materials like chromium salts, which can contaminate soil and water supplies and endanger human health as well as the environment. This work presents a novel approach for the development of leather from sarda sarda fish skin, which is chrome-free, based on vegetable tannins for the tanning process and use fewer chemicals. The procedure applied was able to produce high-quality leather using sustainable products.

Keywords: Fish skin leather; *sarda sarda* fish; vegetable tanning; chrome-free tanning

1. Introduction

In a recent study from 2021(European commision, 2022) has shown that Portugal is the largest fish consumer in the European Union, with approximately 60 Kg *per capita* being consumed annually. This results in around 600 million tonnes of residue, including fish scales, skins, and spines. For *sarda sarda* in particular, 277 tonnes were fished in 2018 along the Portuguese coast, but despite having a surplus of this specific species, this is not directly translated into commercial value.

Nowadays, there is an increasing concern regarding the environmental impact of the leather industry. In fact, around 90% of the leather industry is still using chromium in their traditional tanning processes, and around 40% of the used chromium does not interact with the leather and is discarded in the effluents(Fatema-Tuj-Zohra et al., 2023). On the other hand, vegetable tanning, in opposition to chrome tanning, is recommended due to their biodegradability and decrease in bioaccumulation(Krishnamoorthy et al., 2013).

Based on these recent findings, there has been a shift in the paradigm, guiding the scientific community to search for not only greener alternatives to chromium in leather tanning(Cavali et al., 2022; Fatema-Tuj-Zohra et al., 2023; Hao et al., 2023; Herath et al., 2023) but also to reuse and repurpose fish skin residues from fishing and fish consumption(Herath et al., 2023; Lohay, 2023; A. Pertiwiningrum et al., 2022; Ambar Pertiwiningrum et al., 2022; Sarkar et al., 2023). Tannins are vegetable polyphenolic chemicals that have been useful in a variety of applications, including in the tanning process of leather. These tannins can be extracted from quebracho (Schinopsis lorentzii), which have a considerable concentration of total condensed tannins (122.7mg/g). These tannins can bind to proteins in the skin and stabilize their structure, avoiding the decomposition of skin and increasing the resistance.(Fraga-Corral et al., 2020)

In this work, we present a novel protocol for leather production using *sarda sarda* fish skin as raw material. This procedure involves chrome-free reagents such as mimosa and quebracho extracts in the tanning process. The hides produced using this protocol demonstrate potential as a prototype for application in the leather industry.

2. Materials and methods

Ammonium sulphate and formic acid were purchased from Carlo Erba reagents (Emmendingen, Germany). Sodium Bisulfite 40% (w/v), sodium chloride and sulphuric acid were purchased from Panreac (Barcelona, Spain). Sodium formate was prepared in situ in our laboratory by adding 1 equivalent of NaOH to 1 equivalent of formic acid on an ice bath. The mimosa and quebracho extracts were obtained from Sanderma (Alcanena, Portugal). Calcium hydroxide was purchased from VWR chemicals BDH (Radnor, USA). Sodium carbonate was purchased from Merck (Darmstadt, Germany).

The tanning process was performed using an IBELUS dyeing machine IBELUS IL-720 (both 1 and 12 recipient apparatus).

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Shimadzu IRAffinity S1, performing 40 scans between 400-4000 cm^{-1} wavelength, at a resolution of 8 cm^{-1}. Optical microscopy was performed using a Microscope Leica DM750 M (brightfield), coupled with a Hugh-definition digital camera. The mechanical properties were measured using a dynamometer Hounsfields H100KS with the QMat (3.51) software, following the BS EN ISO 2062:1995 standard.

3. Results and discussion

The hides were fleshed, and then submitted to the pre-tanning and tanning protocols described in Figure 1. Briefly, the skins were submitted to 10 stages: Soaking, Liming, Deliming, Bating, Pickling, Tanning, Neutralization, Retanning/Dyeing, Greasing, Fixing, since greasing and fixing are performed at the same stage.

The first step in the tanning process is the soaking phase, which aims to create space between the fibres and remove impurities from the surface of the hide. This is followed by liming, performed with "milk of lime" ($Ca(OH)_2$) to remove hair and other keratinous materials. This loosens the collagen fibres, improving skin swelling and thus improves its flexibility after tanning. At this stage, the remaining flesh that may have remained on the skin is removed. Then, during deliming, the lime is removed, and the pH is adjusted by using ammonia-based compound. The following step is called Bating, where the hide is softened, flattened, and tenderized using proteolytic enzymes at a specific pH that is related to the specific enzyme used. This is followed by degreasing to remove the fat, naturally present in the hide, using organic solvents. After hide preparation, tanning is performed using tannin extract. At this stage, where collagen fibres are converted into a stable material. The stabilization is obtained via additional cross-linkages by reactions between the tannins and the collagen active functional groups. Finally, the skin is retanned, conferring an additional levelling/homogenization to the hide, as well as additional filling. This final step can be complemented with additional processes, as for example dyeing, finishing and greasing.

In each step, the conditions were optimized to account for the raw material specificities (thickness, degradability, etc). The quantities of each reagent were defined as a percentage of the total weight of the skin

In each step, the conditions were optimized to account for the raw material specificities (thickness, degradability, etc). The quantities of each reagent were defined as a percentage of the total weight of the skin. A rigorous pH control is necessary to assure that the desired phenomena (fiber opening, fiber swelling, tannin fixation) can occur.

The optical microscope images showed the outside of the fish before and after the tanning process. The cellular arrangement shows the shape of small scales, an intrinsic characteristic of this species. In the tanned skin, there is a noticeable thickening of the skin that does not allow light to pass through so easily. The brownish colour evidenced the uniform penetration of the tannins into the dermis after the tanning. Moreover, melanophores found between the dermis and hypodermis before the tanning process on the fish skin were completely covered after the tanning, showing the efficiency of quebracho in stabilizing the skin (Figure 2).

The FTIR spectrum of the tanned fish skin was obtained (**Figure 3**) and is in accordance with the literature(Chae et al., 2022; Elbialy et al., 2020). The obvious band at 3300 cm^{-1} was attributed to amide A and B generated due to the stretching vibration of N-H in collagen. The broadening of this signal is attributed to the presence of retained water within the material, as expected due to swelling and natural retention. The stretching vibrations of alkyl groups are located at 2920 and 2850 cm^{-1}. Moreover, the asymmetric and symmetric stretching vibrations of the carboxylate groups in the skin emerged at 1651 and 1454 cm^{-1}. The characteristic bands assigned to sulfate groups were detected around 1234 cm^{-1}. The band at 1031 cm^{-1} was assigned to C-O stretching vibrations.

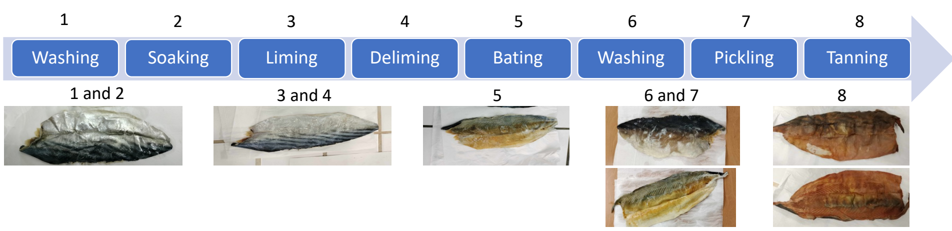


Figure 1. Fish skin tanning protocol for pre-tanning preparation of raw hides.

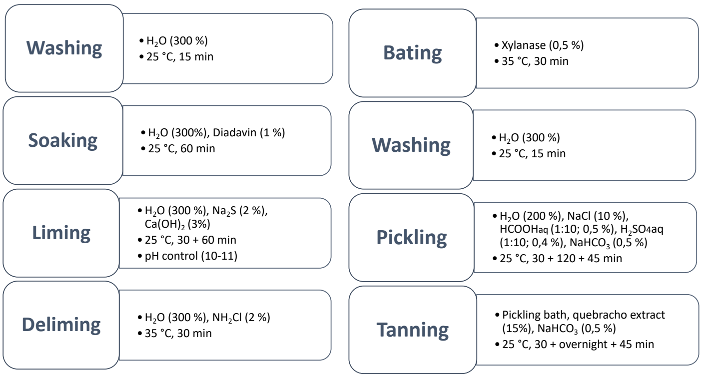


Figure 2. Microscope images of the raw and tanned skin.

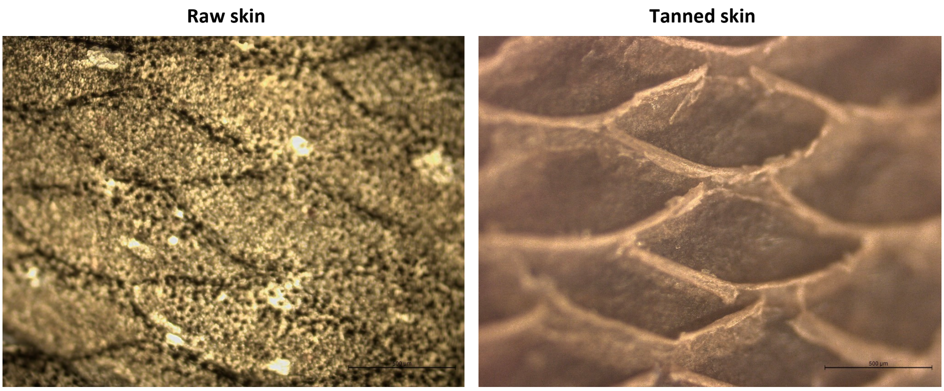
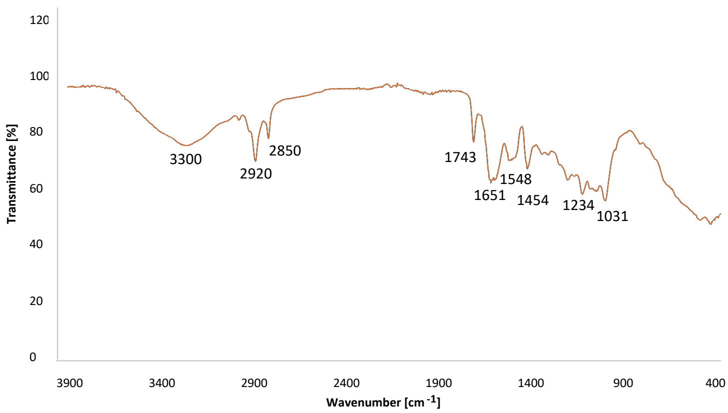


Figure 3. FTIR of the tanned fish skin with quebracho extract.



4. Conclusion

In this work, a simple procedure for the preparation of fish skin leather hides was developed. This procedure involved quebracho and mimosa extracts, removing the chrome-based reagents in the tanning process. The prepared samples demonstrated adequate physico-chemical properties, demonstrated by the FTIR spectra and electronic microscopy images, and are in concordance with the literature. Thus, the samples obtained can be considered a good proof of concept for this methodology, and a good impulse for further process and prototype optimization.

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